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USE OF CAPTURED CEMENT DUST FOR MAKING MASS-USE GLASS

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It is shown that there is promise in using dust from electric filters, which are used in cement production, for making sheet (heat-insulating) and container glass. Adding 5 – 15% dust to the batch makes it possible to decrease or eliminate the use of natural and artificial material without degrading the quality of the glass with respect to gas-containing inclusions. As the dust fraction increases the equilibrium of the oxide forms of iron in the glass shifts in the direction of higher degree of oxidation, which is explained by the presence of sulfur containing compounds.

Key words: salvaging of wastes, cement dust, mass-use glass, spectral characteristics, equilibrium oxide forms of iron, chemical need for oxygen in the batch.

The problem of reducing the cost of mass-use glass (sheet, container) while preserving or improving its equality is a key problem in a market economy. The best way to reduce the production costs is to use in the technological process wastes from other industries [1].

It is well known that cement production generates large quantities of dust. Dust formed during the preparation of the initial mix, calcination of clinker and pulverizing cement, is ordinarily returned into production. However, this is a forced step, as a result of which the properties of the material can be degraded because of the accumulation in it of alkali-metal oxides which have a negative effect on the strength of concrete block [2].

Successful use of wastes requires that their composition be close qualitatively and quantitatively to that of the products from industries where the use of wastes is planned. On this basis it is desirable to use the dust from cement production in glassmaking technology.

The present work studies the possibility and prospects for using captured dust from cement production for making glass.

Considering the high content of iron oxide in cement dust, compositions of sheet heat-insulating (composition 1) and container (PT glass — composition 2) (Table 1) were chosen for this study.

The batch was made using raw materials with the following content (%)[5] of iron oxide (III): sand — 0.022; feldspar concentrate (FSC) — 0.3; dolomite — 0.2; chalk — 0.08; soda — 0.006. In addition, 5, 10, or 15% cement dust was added to heat-shielding glass and 5% electric-filter dust from cement product (CD) in Novorossiisk was added to container glass. The composition of the dust in terms of dry matter was a follows (%): 21.91 SiO_2, 4.41 Al_2O_3, 4.01 FeO_3, 63.60 CaO, 0.68 MgO, 2.28 SO_3, 0.53 Na_2O, and 2.58 K_2O.

Marl was used at the enterprises in Novorossiisk to obtain clinker — carbonate – clayey sedimentary rock to which pyrite cinders were added.

The calculations showed that using such a product in the preparation of glass batch will make it possible to decrease partially or completely the use of conventional materials with

[5] Here and below — content by weight.

TABLE 1. Compositions of Experimental Glasses

Glass	Content, wt.%			
	SiO_2	Al_2O_3 + Fe_2O_3	CaO + MgO	Na_2O + K_2O
Composition 1 — heat-absorbing*	72.5	2.1 (Fe_2O_3 to 0.6)	10.4	15
Composition 2 — PT container glass**	71.6	3.0 (Fe_2O_3 to 0.5)	11.0	14

* TU 21-2323–72. Heat-absorbing sheet glass.

** GOST R 52022–2003. Glass container for food and perfume-cosmetic products. Glass package.

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100 kg glass obtained as follows: sand by 0.23 – 0.76 kg, feldspar concentrate by 0.73 – 2.11 kg, chalk by 3.59 kg, dolomite by 0.92 – 10.44 kg, and soda by 0.05 – 0.16 kg (Table 2) and thereby decreasing the production costs and making the product more competitive.

Together with the raw materials definite quantities of iron and sulfur (in terms of Fe_2O_3 and SO_3, respectively), which are presented in Table 3, enter the glass.

In mass-use glass obtained from mineral raw materials iron can coexist in two oxide forms — FeO, Fe_2O_3, and in the form of an "amber chromophore," consisting of quadrupuly coordinated Fe^{3+} ion, surrounded by three O^{2-} ions and one sulfide sulfur ion S^{2-} [3, 4]. The spectrum of the trivalent oxide form of iron is characterized by strong absorption in the short-wavelength region of the spectrum and the bivalent spectrum has a wide band in the near-IR region with a maximum near 1000 – 1100 nm (Fig. 1*a*). The amber chromophore manifests in the spectrum of the glass as a quite intense band at 440 – 460 nm (Fig. 1*b*). The appearance of the amber chromophore is possible under strongly reducing conditions.

According to the data in [3] (Table 4) the iron considered here forms the following series in order of increasing absorption in the visible region of the spectrum: $Fe^{3+} \rightarrow Fe^{2+} \rightarrow$ amber chromophore.

The equilibrium position of the oxide forms Fe(II) ⇄ Fe(III) depends on many technological factors [5] among which are the following: the iron concentration in glass; oxidation-reduction potential of the raw materials and batch; the presence of other variable-valence elements (for example, sulfur with sulfate fining).

Natural raw materials and wastes from other industries used for preparing glass batch are contaminated to one degree or another by reducing impurities which make an additional contribution to the shift of the iron equilibrium in the FeO direction, degrading the color of the glass and complicating the glassmaking process.

To take this factor into account the amount of oxygen required to oxidize the reducers and impurities in the raw material and batch [6] — the chemical requirement for oxygen (CRO) by the method of bichromatometry or permanganometry — is calculated analytically.

TABLE 2. Batch Prescription for Composition 1 Glass

Component	Component mass, kg/100 kg glass composition 1* with CD content in the batch, %			
	0	5	10	15
Sand	68.25	68.02	67.76	67.49
FSC	6.27	5.54	4.85	4.16
Soda	25.19	25.14	25.08	25.03
Dolomite	16.46	15.54	10.77	6.02
Chalk	3.59	0	0	0

* Sodium sulfate was not used for preparing batch.

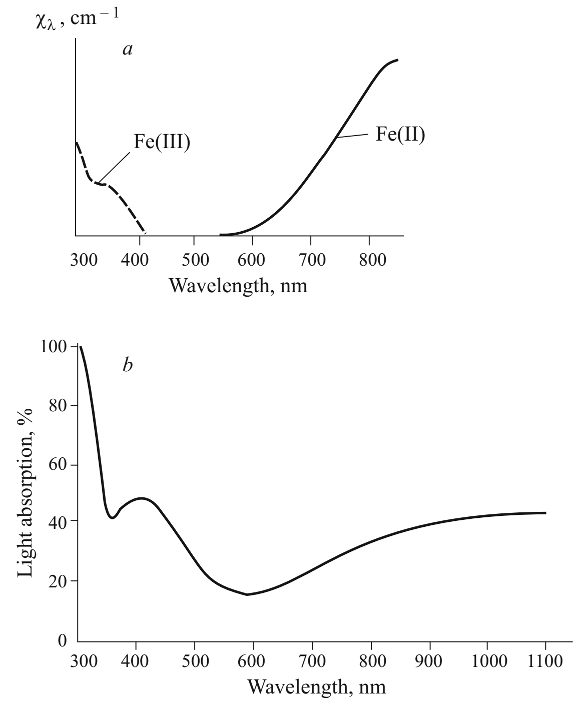

Fig. 1. Absorption spectrum of silicate glasses colored by iron: *a*) bi- and trivalent; *b*) amber chromophore.

Let us examine the results of the determination of the CRO of raw materials used for making composition-1 experimental glasses.

CRO of the raw materials and batch

Material:
- sand 92.0
- FSC 70.0
- dolomite 106.3
- CD 160.0
- soda 20.0
- chalk 133.0

Batch with CD content, wt.%
- 0 . . . . 94.3
- 5 . . . . 95.9
- 10 . . . . 99.0
- 15 . . . . 101.3

It should be noted that chalk and CD have the highest CRO. This is probably explained by the sedimentary origin

TABLE 3. Sulfur and Iron Content in the Composition 1 Glass

CD content in batch, %	Content, wt.%	
	Fe_2O_3	SO_3
0	0.07	0
5	0.21	0.09
10	0.35	0.17
15	0.49	0.26

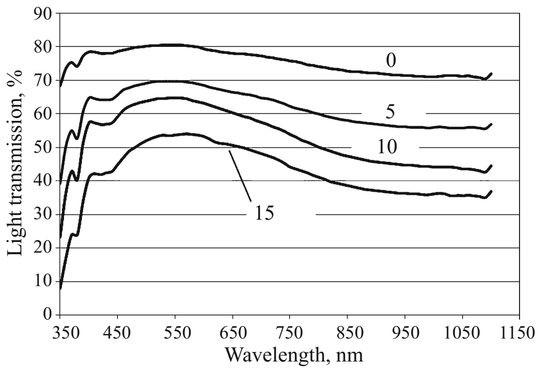

Fig. 2. Spectral light-transmission curves of composition-1 glass (the CD content (by weight) in the batch is indicated on the curves).

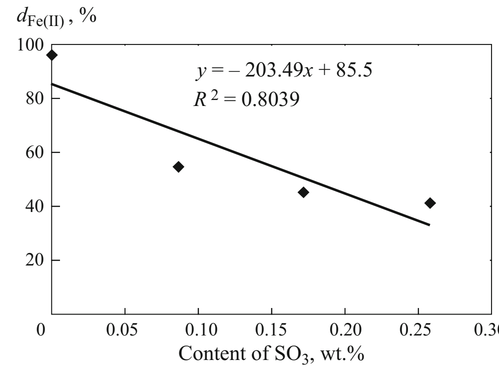

Fig. 3. Plot of the fraction of bivalent iron versus the SO_3 content in a batch of composition-1 glass.

of chalk and marl. Soda is a technical product, produced chemically and purified during production, has the lowest chemical requirement for oxygen, as should be.

The CRO for batches vary only by 7% (94.3 for initial and 101.3 for batch with 15% CD), so that one can suppose that the batch will have a very insignificant effect on the iron equilibrium in glass.

Glass was made in corundum crucibles in a laboratory electric furnace with silit heaters. No fining agent (sodium sulfate + carbon) was introduced into the batch, since the SO_3 content in the cement dust was substantial.

The spectral transmission curves of compoistion-1 glass samples, 4 mm thick, are displayed in Fig. 2.

The successive decrease of the visible-light transmission (wavelength 550 nm; 80 and 55% decrease, respectively, for the initial glass and glass synthesized from batch with 15% CD) is explained mainly by the higher content of total iron introduced into the glass with a higher fraction of cement dust.

In the near-IR region of the spectrum a successive decrease of the light transmission with increasing CD concentration in the batch is also observed in the absorption band of bivalent iron (950 – 1050 nm). This is explained by an increase of the iron oxide (II) content as a consequence of an increase of the total iron content as well as by a possible left-ward shift of the equilibrium Fe(II) ⇄ Fe(III).

TABLE 4. Properties of Different Forms of Iron in Glass

Ionic form of iron	Absorption band, nm	Coefficient of absorption per unit length (cm^{-1}/% oxide mass)	Glass color
Fe^{3+}	380	1.27	Light brown
	420	0.35	
	435	0.34	
Fe^{2+}	1050	9.10	Blue
Sulfoferrite (amber chromophore)	~ 410	Very high	Amber-brown

To evaluate the probability of a displacement of the equilibrium, fractions of the bivalent iron $d_{Fe(II)}$ were calculated from the expression

$$d_{Fe(II)} = \frac{-\log \tau_\lambda - 2D_{\rho m}}{l m_{Fe(tot)} \rho \varphi_{\lambda, Fe(II)}} \times 100\%,$$

where τ_λ is the transmission of the glass sample at the wavelength 800 or 1000 nm, arb. units; $D_{\rho m}$ is a correction for multiple reflection; it is neglected for mass-use glass containing substantial concentrations of coloring elements; l is the thickness of the glass sample, cm; $m_{Fe(tot)}$ is the total iron concentration in the glass in terms of the metal, wt.%; ρ is the density of the glass, g/cm^3; $\varphi_{\lambda, Fe(II)}$ is the volume indicator of the absorption by bivalent iron in terms of the concentration (for wavelengths 800 and 1000 nm it assumes the values 2.25 and 3.60 cm^2/g, respectively).

The calculation showed that the ferrous fraction of the iron decreases with increasing CD content in the batch as follows.

CD content in batch, wt.%	$d_{Fe(II)}$, %
0	96
5	55
10	45
15	41

Therefore introducing CD shifts the equilibrium Fe(II) ⇄ Fe(III) rightward. This is explained by basic factors:

– increase of the content of total iron in glass [8];

– successive increase of the sulfur-containing compounds acting on iron as an oxidizer in accordance with the reactions [3]

$$Fe(II) \rightarrow Fe(III); \quad S(VI) \rightarrow S(IV).$$

Indeed, as Fig. 3 shows, a proportional relation is observed between the values of $d_{Fe(II)}$ and the concentrations of sulfur compounds in the glass in terms of SO_3.

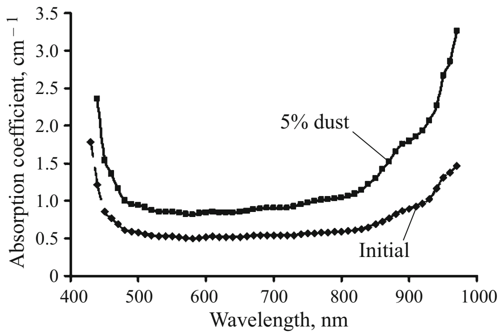

Fig. 4. Spectral curves of the absorption coefficient of PT glass (composition 2).

An identical calculation of the ferrous fraction content performed with the spectral curves of the absorption coefficient of composition-2 container glass (Fig. 4) showed that $d_{\mathrm{Fe(II)}}$ is 90% in the initial glass 51% in glass synthesized from batch with 5% CD added. Therefore, irrespective of the application of a glass the introduction of CD into its batch shifts the iron equilibrium in the direction of the oxide (III) form.

The basic results of this work can be summarized as follows.

The presence of sulfur-containing compounds in CD makes it possible to do completely away with sodium nitrate without affecting the fining quality of the glass.

The CRO of dust from the electric filters used in cement production is higher than in the conventional materials, but this has a negligible effect on the CRO of batch with up to 15% CD added.

As the CD fraction in the batch increases, the equilibrium of the oxide forms of iron in the glass shifts in the direction of the highest degree of oxidation. This is explained by the presence of sulfur-containing compounds in the cement dust.

The introduction of dust from electric filters use in the cement industry into the batch for making sheet and container glass decreases or eliminates the use of natural and artificial materials.

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